

✓ STUDIES ON SELECTIVE AROMATISATION OF LPG TO BTX USING MODIFIED ENCILITE CATALYST

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY*

by
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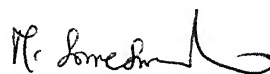
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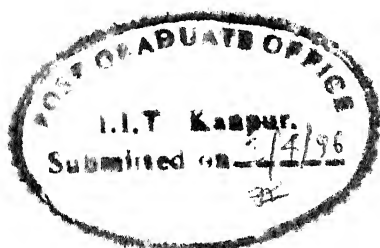
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ABSTRACT

benzene, toluene and xylene (BTX) are the three widely used aromatic chemicals which can be produced by the selective aromatisation of LPG over Zn-encilite catalyst. In this study the effect of operating parameters like temperature, residence time and feed composition on the conversion of LPG, selectivity and yield of BTX has been investigated. Detailed kinetic modelling is done in order to determine the rate controlling step and the corresponding rate constants and the activation energy have been calculated.

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NOMENCLATURE

A	= Benzene, toluene and xylenes (BTX)
A(i)	= Area measured by integrator under the peak of the i-th components
B	= Butene/Propene
C_{σ}	= Concentration of the vacant acid sites
C_{σ}^0	= Initial concentration of the acid sites
$C_{B\sigma}$	= Concentration of the adsorbed butane/propane
$C_{O\sigma}$	= Concentration of the adsorbed butene/propene
C_{τ}	= Concentration of the vacant Zn^{2+} sites
C_{τ}^0	= Concentration of the vacant Zn^{2+} sites (initial)
$C_{A\tau}$	= Concentration of the adsorbed aromatics on Zn^{2+} sites
$C_{O\tau}$	= Concentration of the adsorbed butenes/propenes on Zn^{2+} sites
F	= Total flow rate of reaction mixture, mol/h
F_B	= Flow rate of butane/propane, mol/h
K_1	= Butane/propane adsorption equilibrium constant, atm^{-1}
K_2	= Thermodynamic equilibrium constant for butane/propene dehydrogenation
K_3	= Butene/propene desorption equilibrium constant on acid sites of Zn encilite catalyst, atm^{-1}
K_5	= Thermodynamic equilibrium constant for butene/propene aromatization
K_6	= BTX desorption equilibrium constant, atm^{-1}
O	= Butene/propene
P_A	= Partial pressure of BTX, atm
P_B	= Partial pressure of butane/propane

P_O	=	Partial pressure of butene/propene
$-r_B$	=	Rate of reaction of LPG, gmol/g-h
S	=	% selectivity towards BTX
Δw	=	Weight of catalyst, g
$W(i)$	=	Known amount of component i
Δx	=	Fractional conversion
Y	=	% yield of BTX
σ	=	Acid sites on the Zn encilite catalyst
τ	=	Zn^{2+} on the Zn encilite catalyst
λ	=	Wavelength of the radiation, \AA
θ	=	Angle which the X-rays leave from the plane of the catalyst, degrees

CHAPTER 1

INTRODUCTION

Benzene, Toluene and Xylene are the three basic aromatic compounds which find extensive applications in many downstream processing industries. These compounds are the starting materials for several reactions, viz., dehydrogenation, cyclisation, oxidation, polymerisation etc.. Benzene is used in the manufacture of various compounds like styrene, phenol, and linear alkylbenzene and maleic anhydride. Toluene is used in the manufacture of tri nitro toluene (TNT), pesticides, chlorinated derivatives, solvents and thinners. Xylenes find extensive use in the production of poly ester fibre, polyester filament yarn, polyester filament resin and films.

Two main sources of aromatics are (i) naphtha reforming (ii) distillation of light crude oil, coke etc.. These processes involve multiple steps and high temperatures. Direct conversion of lower alkanes to aromatics is gaining momentum of late. Popularity of this process is also because it involves alkanes which are available at a lower cost than naphtha. Since LPG contains mainly propane and butanes its use as a raw material for the production of aromatics has many advantages over naphtha.

Conversion of LPG to aromatics is preferred over the conversion of either pure propane or butane as the latter involves the cost of purification. Hence the direct conversion of LPG is economically more viable. Aromatization of LPG results in a mixed

BTX aromatics stream and a large volume of hydrogen by-product. Some surplus fuel gas is also produced. One industrial process viz., the Cyclar process has started production in 1990 at Grangemouth in Scotland. It is developed by British Petroleum (BP) in collaboration with Universal Oil Products (UOP). The Cyclar aromatics have properties that make them suitable as a petrochemical grade product and also as a gasoline blending agent.

With the economical liberalisation and also cuts in import duty, the availability of LPG in India is expected to be large in the near future. Many refineries are coming up and some new refineries have started production recently. Hence conversion of low value alkanes to value added BTX will have a bright prospect.

In the aromatization reaction a bifunctional catalyst is used. Mainly ZSM-5 type catalyst with different silica to alumina ratios is used in the reaction. The promoter usually is a non-noble metal like Zn, Ga etc.. Acidic nature of the catalyst is provided by the Zeolite component. The Cyclar process reported around 63-66 wt% of the aromatics yield with LPG. In this process inert binder is used in the metal promoted Zeolite catalyst. This process reported that toluene is approximately 45 wt% of BTX.

The aromatization is a complex reaction which involves dehydrogenation, oligomerization, cyclization, dealkylation and alkylation steps. Study of conversion of propylene into aromatics over H-ZSM-5 catalyst is carried out by Ono et al. (1989), and Wilshier et al. (1987). Guisnet et al. (1992) have studied the selective aromatization of short chain alkane on ZSM-5 catalyst.

The activity and kinetics of n-butane aromatization over new hybrid catalysts have been investigated by Yao et al.(1990) and Mao and Yao (1991). Different promoters have been used in the ZSM-5 but most of them are patented. Various other publications on the effect of different factors and the reaction mechanisms are available (1,2,3,4.).

Recently Jana and Rao (1993 a) have studied the effect of temperature , concentration of feed, contact time and coking by using modified encilite catalyst and pure butane as feed stock. They also carried out optimization studies (1993 b) for maximizing the yield of BTX along with the deactivation kinetics. Extensive publihsed literature is available on the aromatization reaction. Nearly all of them dealt with single pure reactant (propane or butane). However, literature on the aromatization using LPG as the feed stock is rather limited (5,6).

CHAPTER 2

LITERATURE SURVEY

The dehydrocyclodimerisation of propane, butane and pentane has been described by Csicsery(7) using bifunctional catalysts such as platinum-on-alumina and Cr_2O_3 -on-alumina. In dehydro cyclo dimerisation, the aromatic products always contain more carbon atoms than the reactant alkanes. The aromatisation of propane and n-butane in the presence of a catalyst is a rather complex process. Mainly ZSM-5 zeolites doped with zinc, gallium, platinum and several transition metal atoms and bimetallics along with metallosilicates having the same pentasil pore opening structure, have been used by several researchers as an active catalysts for the alkane aromatisation reaction. The yield of aromatics depends on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the nature of the exchanged metal ion in the ZSM-5 and on the operating conditions.

The selective aromatisation of propane and n-Butane to Benzene, Toluene and Xylene (BTX) has been reviewed recently by Guisnet et al.(8) and Ono(9). A large no. of publications (10- 12) appeared in the last decade trying to elucidate the role of different dope metal atoms and the acidic properties and also the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the ZSM-5 zeolites which ultimately affect the yield of BTX. The reaction pathway and the mechanism of these reactions have been studied by few investigators (13- 14). Recently Mao et al. (15) have reported the kinetics of the production of BTX from n-Butane.

2.1. Propane and n-butane conversion

Several investigators used ZSM-5 and metal ion exchanged ZSM-5 zeolites as catalysts. Mole et al. have studied this reaction using H-ZSM-5 and Zn-ZSM-5 zeolite at temperatures in the range of 730-820 K. Zn-ZSM-5 shows a higher propane conversion (35%) and better BTX selectivity (63%) than its protonic form. Kitagawa et al.(16) have investigated the effect of Ga ion in Ga-ZSM-5 on the yield of aromatics. On incorporation of both the total conversion and the selectivity of aromatics were enhanced. The selectivity and yield for aromatics reached 70% and 60% respectively at 500°C over Ga-ZSM-5. The role of platinum and the method of incorporation in the synthesized ZSM-5 (Si/Al=40) on the conversion and product distributions of propane aromatisation reaction were investigated by Inui et al.(17). They also reported the role of platinum in Pt/Ga-silicate catalysts of several Si/Ga ratios.

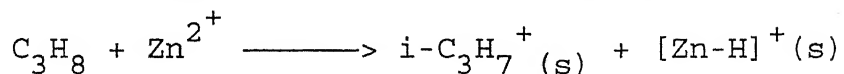
Csicsery(18) reported the dehydrocycloolimerisation of butanes over platinum on an acidic alumina catalyst. The aromatics formed from the butanes are mainly toluene and xylene with small quantities of benzene. Csicsery(19) also investigated the effect of Cr, V, Mo and Mn on the yield of aromatics. Scurrrell(20) studied the conversion of propane, n-butane and i-butane over Zn-ZSM-5 zeolite catalysts at 0.1 MPa and 500°C reaction temperature.

Most of the papers dealt with rate mechanism and reaction steps. Very few studies have been reported on optimisation studies. Jana and Rao(21 - 22) studied the optimisation of the operating parameters using Response Surface Methodology(RSM). Using

encilite catalysts (ZSM-5 with Si/Al=76), they reported that the maximum yield of BTX to be 66 wt% at a temperature of 560°C, feed composition of 11 mol% in n-butane and N₂ mixture and a contact time of 3.37 g hr/mol. They also investigated the mechanism of deactivation of Zn-encilite catalysts (1994 a) and concluded that a small amount of deactivation was observed due to the pore-mouth poisoning after 10 hr of reaction time.

2.2. Role of metal catalyst

Ono et al. (1987) have observed that for propane and higher alkanes, cracking of starting hydrocarbon takes place on the acid sites and the metal ion acts as a catalyst for dehydrogenation of olefine intermediate. Gnep et al. (1987), using Ga-ZSM-5 observed that Ga ion helps dehydrogenation and acid sites help the oligomerisation and cyclisation reactions. Mole et al. (1985) proposed that the Zn cation in Zn-ZSM-5 acts as a hybrid acceptor to give a transient species such as [Zn-H]⁺

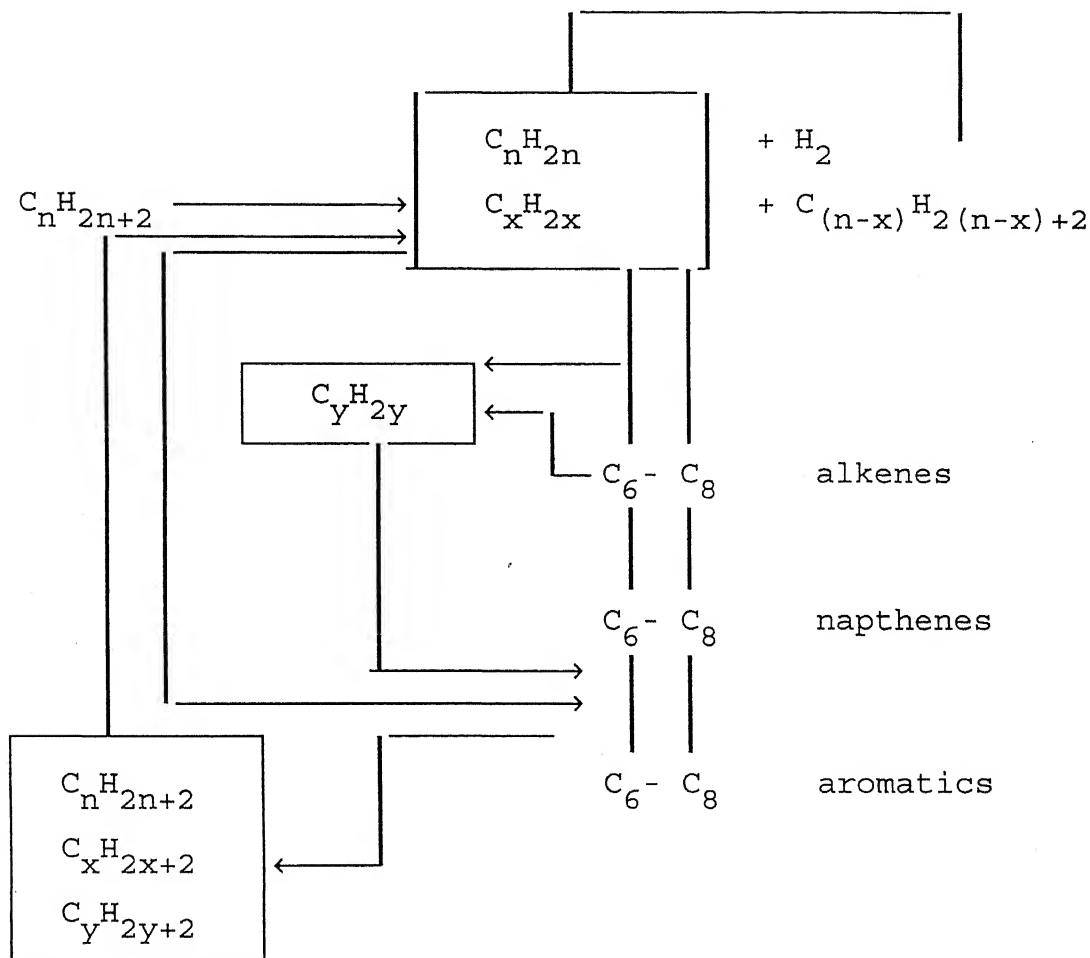


It is reasonably well established that ZnO can produce heterolytic cleavage of C-H bonds to give species of type [Zn-H]⁺. It was reported that Pt in ion-exchanged gallium silicate (Pt/Ga-silicate) plays an important role in dehydrogenation of alkanes to alkenes.

2.3) Reaction pathways and mechanism for propane and n-butane aromatisation

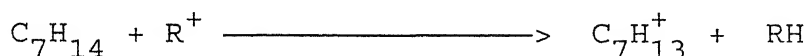
The chemistry of the aromatisation reaction has been suggested by different researchers. Csicsery (1970) described dehydrocyclodimerisation reaction over Pt and Pt group of metals

on alumina or oxides of Cr, Mo, V and W. Most of the reaction mechanisms and rate steps are based on the type of by-products formed. In general, the aromatisation of light alkanes with $n=2-4$ can be explained by the mechanism proposed by Guisnet et al. (1992) as follows:



The first reaction is the formation of C_nH_{2n} alkene by dehydrogenation of corresponding alkane or that of a similar alkane or smaller alkane by cracking. This reaction occurs through the carbonium ion intermediates. These olefines undergo

oligomerisation in presence of acid catalyst through carbenium ion intermediates. The oligomers formed may also crack into C_2 - C_5 alkanes. The C_6 - C_8 alkenes undergo cyclisation inside the zeolite pores and forms naphthenes. The cyclisation occurs only from olefinic carbenium ions. These olefinic carbenium ions formed through hydride transfer from an alkane to a preexisting carbenium ion



Finally , naphtenes formed by cyclisation of long chain alkanes are dehydrogenated to aromatics. The reaction is promoted by light alkenes.

2.4 Objectives of the present investigation :

It is clear from the literature that extensive studies are available on the aromatisation reaction involving pure propane or butane. The literature available using LPG as the feedstock is rather scarce.

The objectives of the work are :

(i) To study the effect of temperature ,feed composition and residence time on selectivity and yield of BTX and also on the LPG conversion to BTX.

(ii) To do kinetic modelling in order to find out the rate controlling step and the corresponding rate constants and activation energy.

CHAPTER 3

CATALYST CHARACTERIZATION

The activity and selectivity of Zn-encilite catalysts are related to their solid state properties like surface area, crystal structure, nature of the acid sites (Bronsted and Lewis), strength of the acid sites, and amount of exchanged metal. Such properties aid in understanding the catalytic behaviour of the solid and elucidating the reaction mechanism.

The catalysts used in the present study were characterised in terms of their surface areas , charateristic X-ray diffraction patterns, nature of the acid sites.

3.1 X-Ray Diffraction Patterns (XRD)

Powder samples were studied for XRD patterns (2θ vs intensity). The test sample was taken in a REICH-SEIFERT ISO-DEBYEFLEX 2002 diffractometer and the XRD patterns were obtained using Nickel filtered CuK_{α} ($\lambda = 1.5405 \text{ \AA}$) radiation. The operating conditions are set as :

Current/voltage = 20 mA/30 KV; scanning speed = $1.2^{\circ}/\text{min}$ in 2θ ; counts per minute = 20 K; time constant = 10 s; chart speed = 0.6 cm/min ; detector slit width = 0.3 mm ; scaning range = $8-50^{\circ}$ in 2θ .

Figure 1 shows the superimposed X-Ray diffraction pattern of Zn-ZSM-5. The characteristic X-Ray peak of Zn-ZSM-5 in the range of $22-24^{\circ}$ is broad due to fine crystallite size.

3.2 Infrared Spectroscopic Studies (IR)

The nature of the acid sites was investigated by using IR spectra of the pyridine adsorbed sample. Perkin -Elmer FT-I series 1600 spectrometer working in the range of $4000-400\text{ cm}^{-1}$ was used. The catalyst was pressed into self-supporting wafers and placed in the stainless steel IR-Cell fitted with KBr windows. The nature of the acid sites was investigated by using IR spectra of the pyridine adsorbed samples. The adsorption band was obtained in the region of 1542 cm^{-1} , 1500 cm^{-1} and 1453 cm^{-1} as shown in the Figure 2. The band at 1542 cm^{-1} characterizes the bronsted sites and it is attributed to C-C stretching vibration of the Pyridium ions. The band at 1453 cm^{-1} indicates the presence of Lewis acid sites which arises from the C-C stretching of a coordinatively bonded pyridiene complex.

3.3 Morphology :

JEOL JSM 840 A scanning electron microscope (SEM) was used to take images (secondary electron image) of Zn-enciliite. The fine powder of sample coated with carbon was ultrasonicated in acetone and a drop of suspension was poured on the stainless steel stub.

As shown in the photograph 3, the catalyst particles are highly intergrown crystals of an overall ellipsoidal shape and of $0.5-1.5\text{ }\mu\text{m}$ diameter with numerous facets and pores.

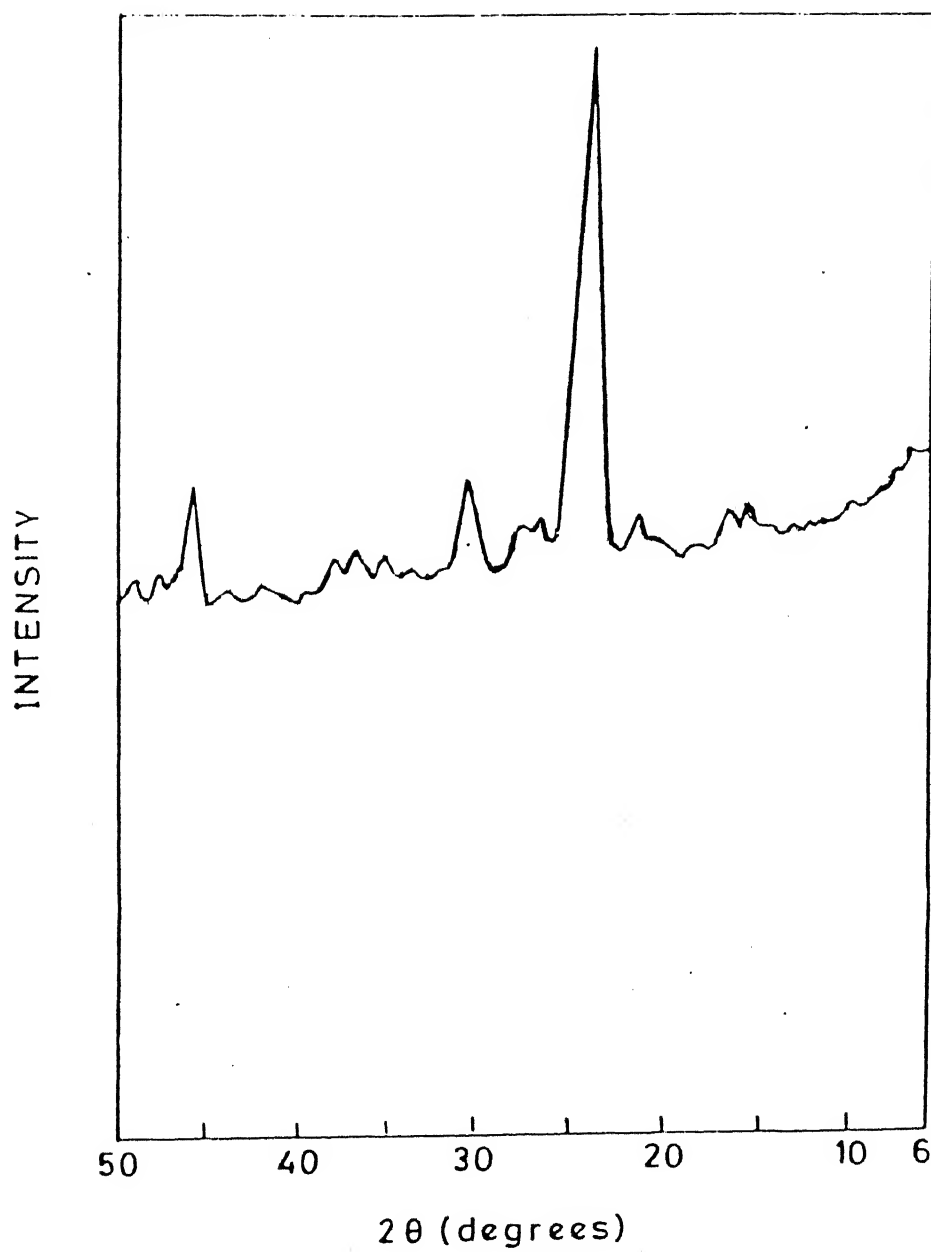


Fig 1. X-Ray Diffraction Pattern of Zn-ZSM-5

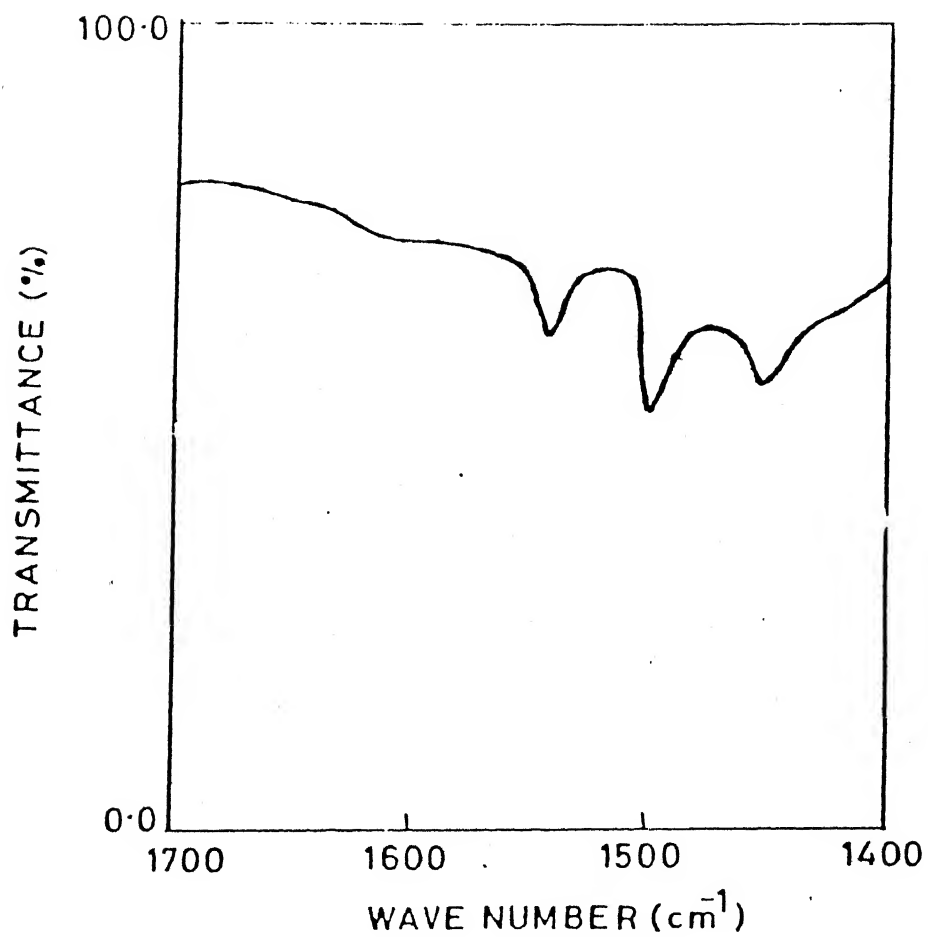


Fig 2. Infrared Spectra of Zn-ZSM-5



Fig 3. Secondary Electron Images of Zn-ZSM-5

CHAPTER 4

MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURE

4.1 Catalyst

The encilite catalyst has been supplied by IPCL, Baroda. The following reagents were used in the preparation of the catalyst:

Zinc nitrate [Zn-NO_3] : It has the minimum assay of 98.5 %. This was obtained from the Loba-Chemie, Bombay.

Ammonium nitrate [$\text{NH}_4\text{-NO}_3$] : This chemical has the minimum reported purity of 99.5% and was obtained from Loba-Chemie Bombay.

4.2 Gases

LPG gas : The LPG (liquefied petroleum gas) of commercial grade has been used in the reaction.

Air : An oil-free rotary compressor with a teflon seal was used to compress air. A cylinder (surge tank) is provided for the air before passing through the Soap-bubble column.

N_2 : Technical grade N_2 was supplied by Triveni Gas Agency Limited, Kanpur which has a minimum purity of 99.5 vol %.

Pure gases for analysis : Pure gas samples (CP grade) obtained from EDT Research were used for calibration. Pure p-xylol and o-xylol, used for calibration of p-xylene and o-xylene were obtained from Riedel-De Haren, Germany. Pure benzene and toluene were obtained from S.D.Fine-Chem Pvt. Ltd., Boisar For analysis of m-xylene m-xylol was used which was obtained from Fluka, Germany.

4.3 Method of preparation of catalysts

Encilite is a ZSM-5 type catalyst with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 76. The details of the method of preparation of Zn-encilite catalyst were as follows. The encilite catalysts were detemplated by heating them in flowing air at 500°C for 12 h. The ammonium form was made by ion-exchanging 30g of the catalyst seven times with a 1.0 litre solution of 1 M ammonium nitrate under reflux conditions with constant stirring by a magnetic stirrer at 80°C for 20 h each time. The exchanged material was filtered and washed thoroughly with distilled water and dried at 30°C . Then it was ion-exchanged with Zinc nitrate. The exchange was achieved by contacting 20 g of NH_4 - encilite with 700 ml aqueous solution of 1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under reflux conditions for 24 h at 80°C while stirring it constantly. The catalyst was then filtered, washed thoroughly with distilled water and dried at 80°C .

4.4 Experimental Set-up

A schematic of the experimental set-up is shown in Figure 4. Compressed air is passed at atmospheric conditions after passing through a column. This was done in order to absorb any moisture. A fine needle valve and a rotameter were used for the control and measurement of flow rate of the incoming air. Similar provision was used for N_2 and LPG. The flow rates were controlled by needle valves and soap - bubble columns were used for the measurement of the flowrates. Silica-gel columns were used to de-humidify the gases. The LPG and N_2 were mixed in a mixing chamber after passing through the Silica gel column. They were preheated to 200°C before going through the reactor. The reactor was a Stainless-

Steel tube of 61 mm length and 10 mm ID. A chromal-alumel thermocouple TC, protected in a 2 mm OD stainless steel sheath co-axial with the reactor tube, was used for measuring the temperature of the reactor at the center. The reactor was placed in a 32 mm ID vertical furnace. A Blue bell temperature controller which operates in the range of 0-1200 °C was used to control the temperature of the furnace. The gas-chromatographic (GC) analysis was carried for the reactor effluents in the chromatograph supplied by CIC, Baroda. After this the reaction products were cooled in a cooler condenser, maintained at 5°C. The cooling water was circulated from a JULABO VC F10 constant temperature bath. The non-condensable hydrocarbons were taken out for further gas chromatographic analysis.

4.5 Experimental Procedure:

In the reactor small amounts of quartz wool was placed at the inlet and outlet respectively. The catalyst was sandwiched between ceramic beads at the inlet and outlet of the reactor. Prior to the reaction, the catalyst was heated in a flowing stream of air for 3h. This step was necessary for the activation of the catalyst. The air flow rate was maintained at 140 cc/min at the reaction temperature. This was followed by the introduction of N₂ for 1h at the reaction temperature. After this the reaction mixture was passed through the reactor via a preheater. Steady state in the effluent composition was achieved 1 h after the reaction started. Then 0.5 cc of the effluent stream was analyzed for the aromatic hydrocarbons. Rest of the effluents were passed through a

cooler-condenser and 0.2 cc of non-condensable gases were analyzed for C_1 to C_4 hydrocarbons and the condensate collected was thrown away. Rest of the gases were vented to the atmosphere through a soap bubble flow meter. At the end of the experiment, the flow of LPG was stopped and N_2 was allowed to pass for 20 minutes.

4.6 Analytical Procedure

The reactor effluents were passed through a heated sampling valve, operated at 200°C , having 0.5 cc sampling loop. The aromatics were separated using 2 m long Bentone on PTO column. These components were analyzed using the GC provided by CIC, Baroda. The gas Chromatograph was fitted with a flame ionization detector (FID). H_2 and air were used to make flame. The following operating conditions were used for satisfactory separation.

Oven Temperature : 70°C
 Injector Temperature : 110°C
 Flow rate of carrier gas : 40 ml/min

The products were mainly BTX. A little amount of higher aromatics were present. The non-condensables were analyzed using a second gas chromatograph supplied by CIC, Baroda. The Column used for the analysis was Durapak of length 3 m, in the FID mode, with following specifications :

Oven Temperature : 41°C
 Injector Temperature : 60°C
 Flow rate : 30 ml/min

* Oven Temperature : 50°C

Injector Temperature : 60°C

DetectorTemperature : 60 °C

Flow rate of carrier gas : 25 ml/min

A Hewlett-Packard 3390 A Integrator was used to measure the responses of the gas chromatographs. The absolute response factor was calculated by following formula

$$\text{abs RF}(i) = \frac{W(i)}{A(i)}$$

where

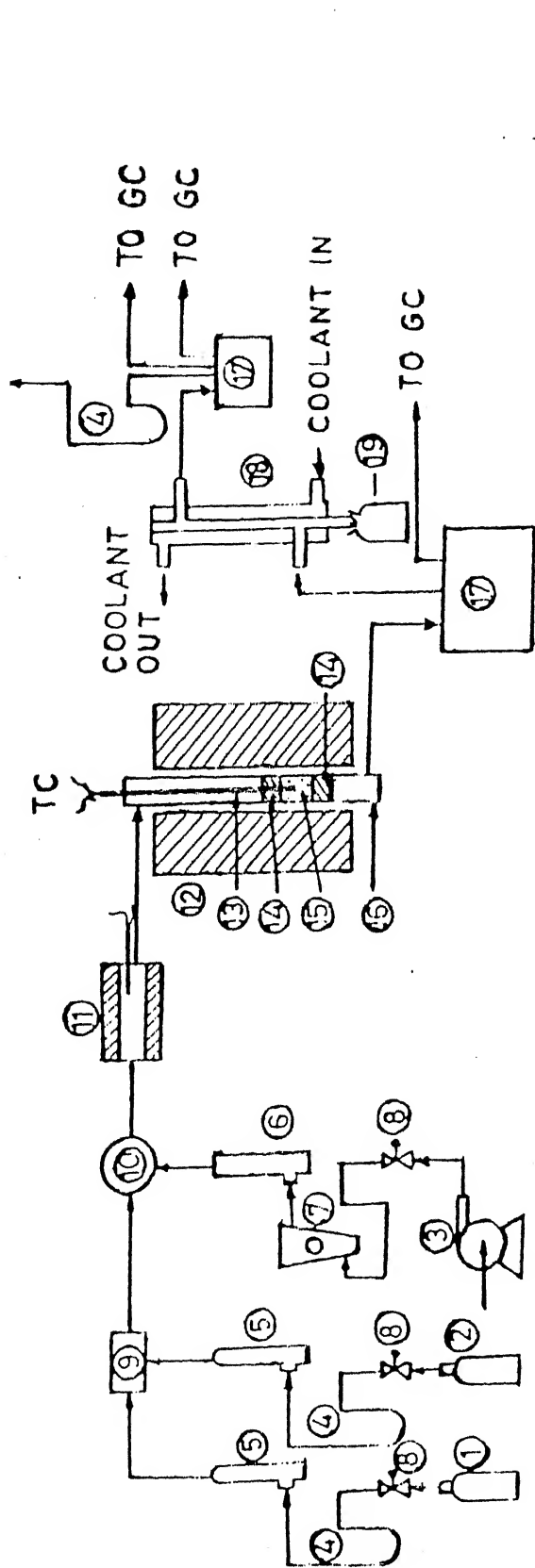
W(i) -- known amount of component

A(i) -- measured area

This gives a factor for each component representing the amount per unit area so as to correct the detector response. The amount of the component in the unknown mixtures were calculated as follows:

$$\text{Amount of "i"} = A(i) \times \text{abs RF}(i) \times \text{Mul.factor.}$$

The values of calibration factors are given in Appendix A



- | | | |
|------------------------------|-----------------------------|--------------------------------|
| ① LPG Gas cylinder; | ② Nitrogen cylinder; | ③ Air compressor |
| ④ Soap-bubble-meter; | ⑤ Packed silica gel column; | ⑥ CaCl_2 drying tube; |
| ⑦ Rotameter; | ⑧ Needle valve; | ⑨ & ⑩ Mixing chambers; |
| ⑪ Furnace; | ⑬ Thermocouple; | ⑭ Quartz wool packing; |
| ⑫ Stainless steel reactor; | ⑮ Gas Sampling valve; | ⑯ Catalyst bed; |
| ⑰ Condensate storage bottle. | ⑱ Cooler-condenser; | |

Fig 4. Schematic Diagram of the Experimental Set-up

CHAPTER 5

RESULTS AND DISCUSSION

The experiments have been conducted using Liquefied Petroleum Gas (LPG). The effect of temperature, feed composition and residence time on conversion, yield and selectivity of LPG to BTX have been studied. Finally, different rate models have been tested using differential reactor data and the corresponding rate parameters are evaluated.

5.1) Conversion of propane/Butane, selectivity towards BTX, and yield of BTX

The conversion of LPG is defined on the basis of its constituents propane and butane respectively. Iso-butane and n-butane are clubbed together.

X = % conversion of propane/butane

$$= \frac{\text{No. of moles of propane/butane consumed}}{\text{No. of moles of propane/butane fed}} \times 100 \quad \dots (5.1)$$

S = % selectivity of BTX

$$= \frac{\text{No. of moles of BTX formed}}{\text{No. of moles of LPG (propane+butane) consumed}} \times 100 \quad \dots (5.2)$$

Y = % yield of BTX

$$= \frac{\text{No. of moles of BTX formed}}{\text{No. of moles of (propane+butane) fed}} \times 100 \quad \dots (5.3)$$

T = % total conversion

$$= \frac{\text{No. of moles of (propane+butane) consumed}}{\text{No. of moles of (propane+butane) fed}} \times 100 \quad \dots (5.4)$$

Also, the selectivity is given by,

$$S = (Y/T) \times 100 \quad \dots (5.5)$$

A model evaluation of conversion, selectivity and yield is given in Appendix B.

5.2 (a) **Effect of reaction Temperature on conversion of LPG**

The effect of temperature on the LPG conversion has been studied in the range of 475 - 550°C. Runs numbered 1-4 represent the effect of temperature and the data are plotted in the Fig.5.

In these experiments the contact time was kept constant at 0.0014 g/(mol/h) and the inlet concentration of LPG was kept at 40%, the rest being nitrogen.

The conversion of both propane and butane increases with temperature as shown in Fig.5. The total conversion also increases with temperature. At any temperature, the conversion of propane is lower than that of butane and the total conversion lies in between that of propane and butane. At a temperature of 550 °C the conversion of butane and propane were 60.67% and 30.83% respectively while the total conversion was 39.86%. From this we can infer that the propane was less reactive for dehydrogenation (from propane to propylene) than butane (from butane to butene).

(b) **Effect of reaction temperature on yield and selectivity of BTX**

The effect of temperature on yield and selectivity was plotted in Fig.6. The selectivity towards BTX decreased with increase in temperature. It was 82.73% at 475 °C and 70.29% at

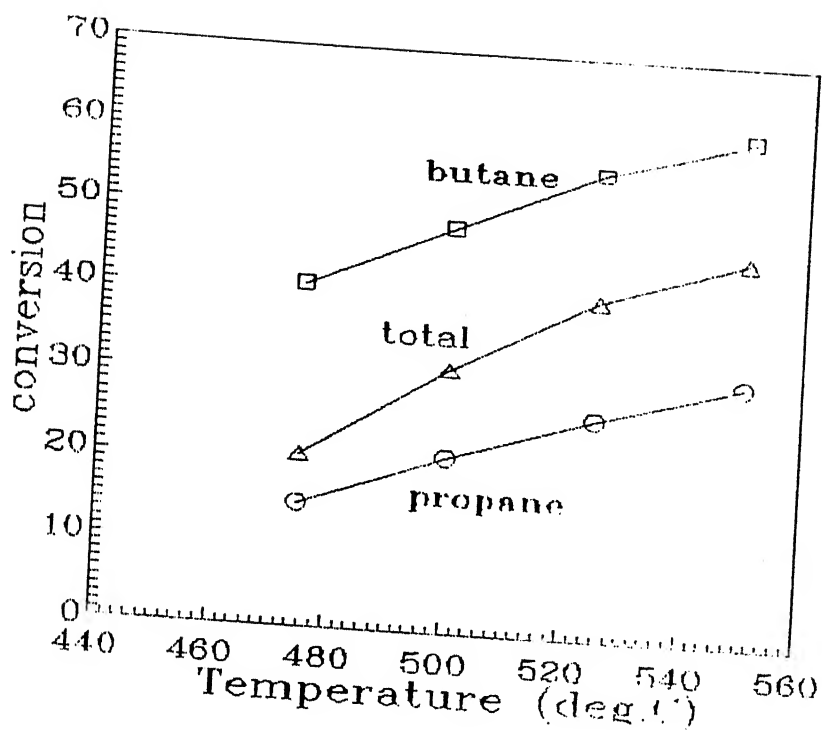


Fig 5 . Effect of Reaction Temperature on the Propane/Butane Total Conversion and their Respective Conversion.

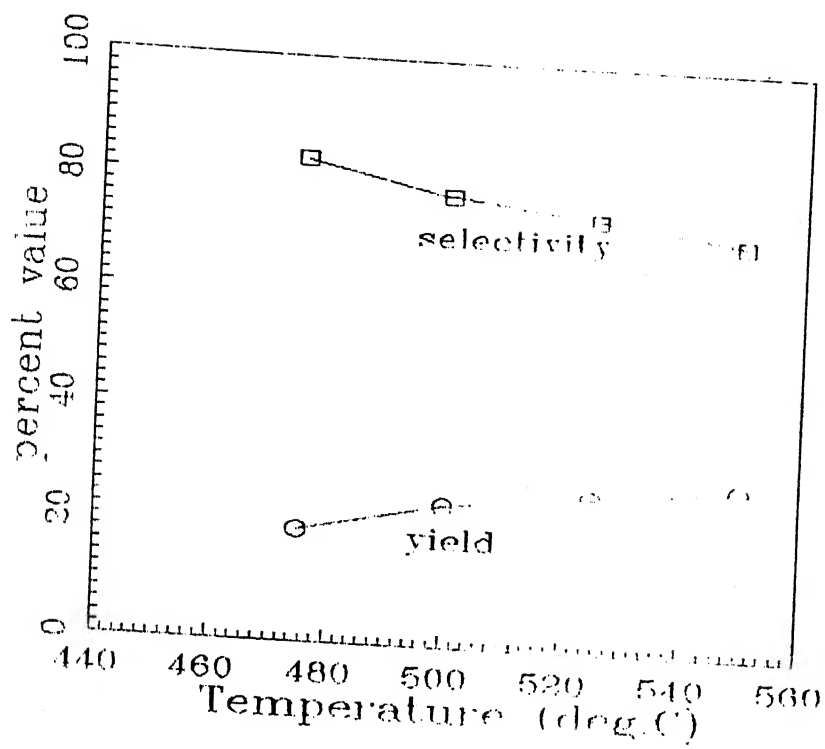


Fig 6. Effect of Reaction Temperature on the Selectivity towards BTX and Yield of BTX

550 °C. The formation of lower hydrocarbon by-products viz., methane, ethane, ethylene etc., increased with temperature which is due to the cracking of C_3 - C_4 alkanes.

The yield of BTX increased with increase in temperature. At a temperature of 475 °C it was 18.63% which increased to 27.97% at a temperature of 550 °C .

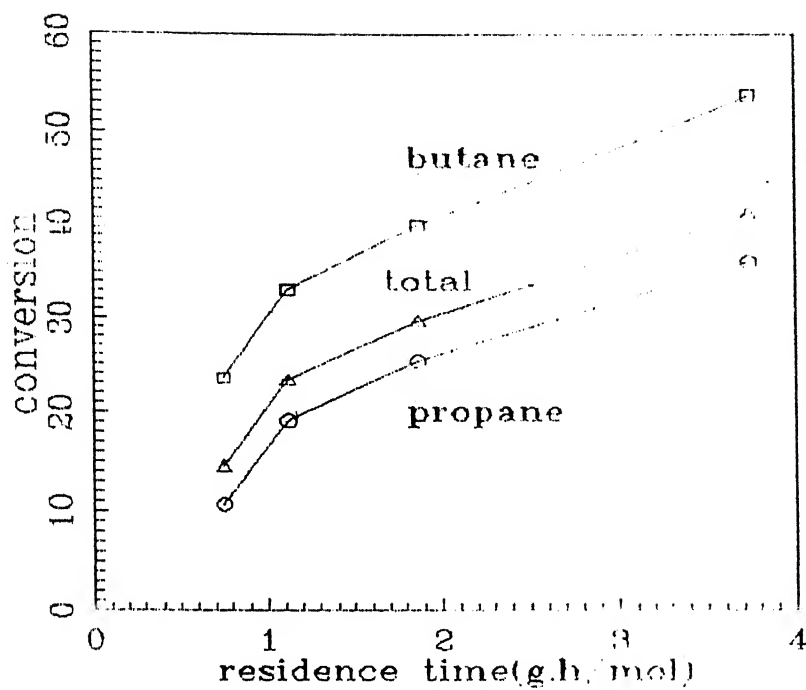
5.3 (a) Effect of residence time on conversion of LPG

The effect of residence time has been studied by keeping LPG inlet concentration at 40 mole%. The temperature was kept constant at 500 °C. The contact time used in the present study ranged from 0.7467 to 3.734 g/(gmol/h). Runs numbered 9 to 12 are plotted in Fig.7. The conversion of propane and butane increased sharply with contact time. The conversion of propane was 10.73% at acontact time of 0.7467 g/(gmol/h) and it increased to 36.19% at a contact time of 3.734 g/(gmol/h). The conversion of butane increased from 23.56% to 53.62% for same change in the contact time. Similarly total conversion also increased from 14.59% to 41.44%.

(b) Effect of residence time on yield and selectivity of BTX

The yield of BTX increases from 11.25% at a residence time of 0.7467 g/(gmol/h) to 26.32% at a residence time of 3.734 g/(gmole/h). However the selectivity decreased with increase in contact time. This is shown in Fig.8

5.4 (a) Effect of feed composition on conversion



**Fig 7. Effect of Contact Time on the Propane/Butane
Total Conversion and their Respective Conversion.**

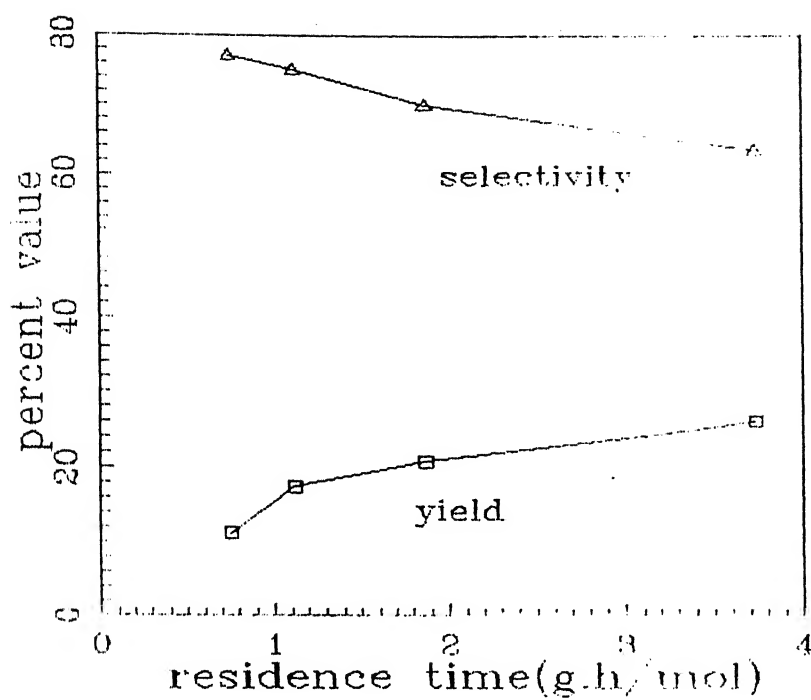


Fig 8 . Effect of Contact Time on the Selectivity towards
BTX and Yield of BTX

The effect of inlet concentration of LPG on conversion has been studied by varying the composition from 33.33% to 75.62 % of LPG in the feed .The reaction temp. was kept constant at 500°C and the contact time was 0.0062 g/(gmol/h). The results (runs numbered 5 through 8) are plotted in Fig.9. Fig.9 shows that the conversions of propane and butane increase with the increase in composition of LPG. The conversion of propane was 20.19% at a feed composition of 33.33% and it increased to 45.67% at a feed composition of 75.62%.of LPG. Similiarly for butane it varied from 62.13% to 84.16% for the same range of concentration variation.

(b) Effect of feed composition on yield and selectivity of BTX

The results are plotted in Fig.10. The selectivity decreased from 62.08% to 45.75% with increase in the feed composition from 33.33% to 75.62%. The yield slowly increased from 20.37% to 26.19% and it can be seen that the feed composition has relatively minor effect on the yield of BTX as compared to selectivity.

5.5 Kinetic study of the main selective reaction of butane/propane to BTX formation.

In accordance with the earlier investigation of Jana (1993) on the aromatisation of n-butane using modified encilite catalysts, the aromatisation of LPG has been postulated to proceed via

1. Dehydrogenation of butane/propane, and
2. Aromatization of propene/butene to BTX

The modelling has been done in the similar lines as proposed by Jana and Rao.(1993a,b). The Dehydrogenation reaction is a

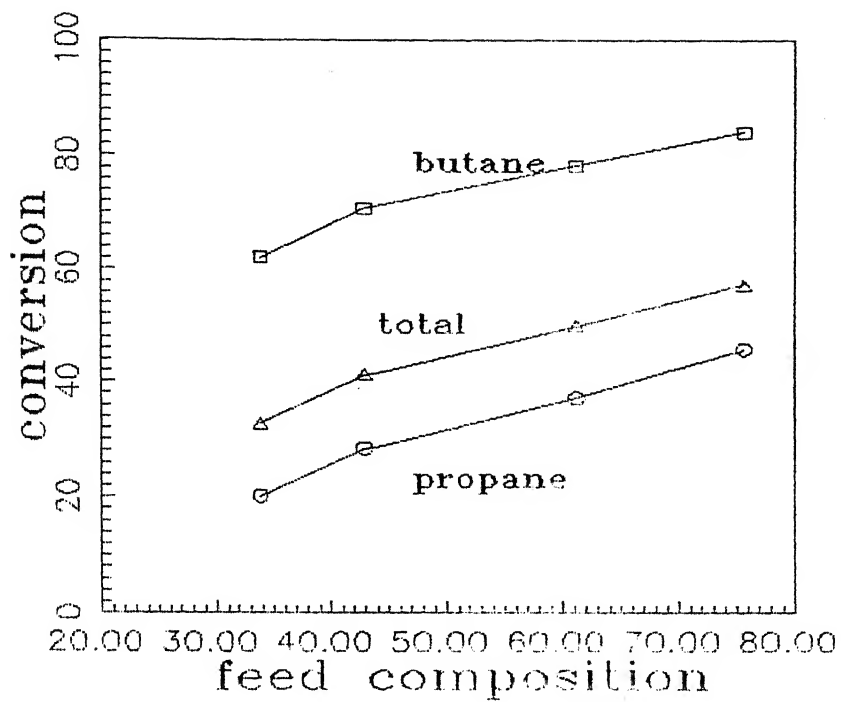


Fig 9. Effect of Concentration of LPG in feed on the Propane/Butane Total Conversion and their Respective Conversion.

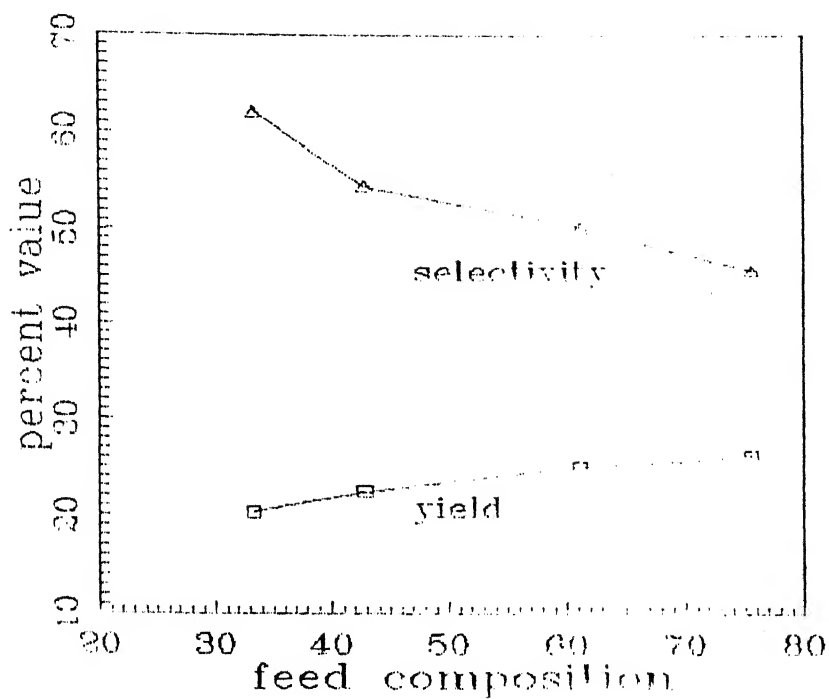
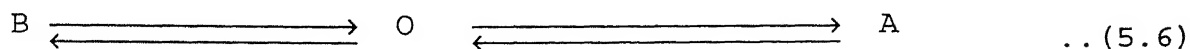


Fig10 . Effect of Concentration of LPG in Feed on the
Selectivity towards BTX and Yield of BTX

reversible reaction in which alkenes may form due to cracking of an oligomer ~~form~~ from alkene as described by Engelene et al. (23). Therefore, the formation of BTX is a consecutive reaction, and both the steps are reversible as shown below



B — butane/propane

O — butene/propene

A — BTX

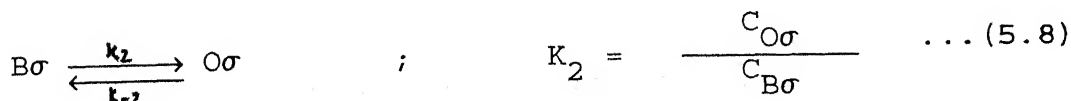
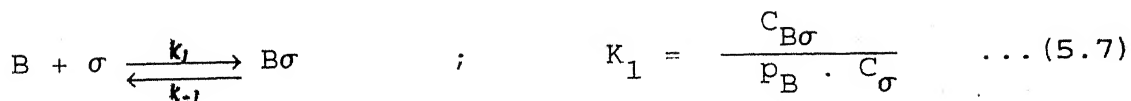
5.5.1 Kinetic models for main selective reactions

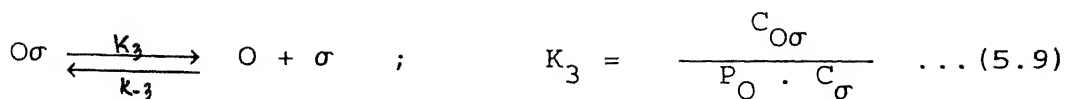
In the development of Langmuir-Hinshelwood reaction mechanism, a distinction was made between active sites σ , which were protonic sites responsible for the dehydrogenation of alkanes to alkenes, and sites τ , which were responsible for aromatization reaction. For the development of kinetic models the following possible rate controlling steps are taken into account :

- (i) the adsorption of the reactant or intermediate,
- (ii) the surface reaction of the adsorbed species, and
- (iii) the desorption of the intermediates or products.

The mechanism of the above proposed reaction scheme is given below:

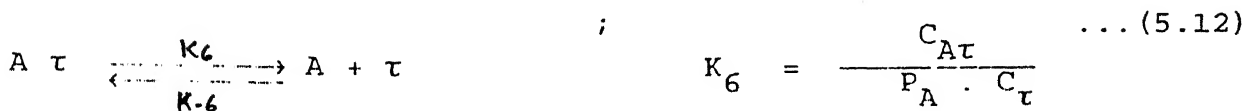
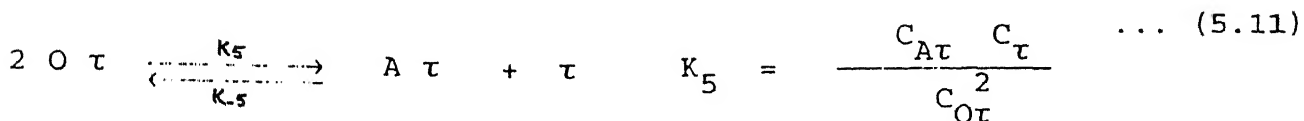
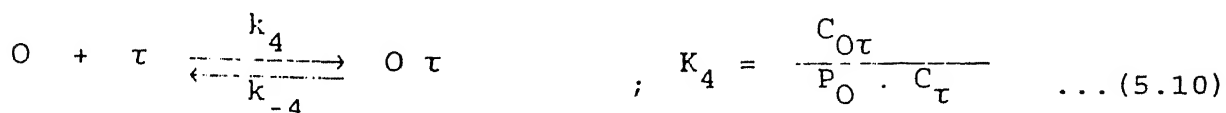
(A) For the dehydrogenation of n-butane to butene on the σ sites,





Where $C_{B\sigma}$ and $C_{O\sigma}$ represents the concentrations of the adsorbed n-butane and butene respectively on the σ sites, and C_σ represents the concentration of the vacant σ sites.

(B) For the aromatization of butene to aromatics on the τ sites,



where $C_{O\tau}$ and $C_{A\tau}$ represent the concentrations of the adsorbed butenes/propenes and aromatics respectively on the τ sites, C_τ represents the concentration of the vacant τ sites.

In all cases, the reverse reaction was accounted for butene/propene. The surface reaction of aromatization was considered to be a reversible one. Taking the above reaction mechanism as a basis, a set of six different rate expressions were developed assuming each elementary step to be rate determining. The rate equations for the above proposed mechanisms are given in Table 9. A sample derivation of Model 5 is given in the Appendix C. The number of parameters for each model is seven. In order to reduce the number of parameters and to avoid numerical problems in analyzing each rate equation, some parameters were clubbed

together as shown in Table 1.

5.5.2 Calculation of Rate Data

Experiments were carried out in differential mode. For this the total conversion was kept very low (below 10%). The rate is calculated by following reaction

$$-r_B = \frac{\Delta X}{(\Delta W/F_B)} \quad \dots (5.13)$$

where

ΔX is conversion

$(\Delta W/F_B)$ is space time

A model calculation of rate from differential rate data is shown in AppendixD. Partial pressures of various components are taken as the average values at the inlet and the outlet conditions.

5.5.3 Estimation of Parameters

The derived rate equations are non-linear with respect to the unknown parameters. In order to evaluate the unknown parameters, a non-linear regression analysis has been carried out. The residual sum of squares (RSS), given by,

$$RSS = \sum_{i=1}^N (R_i^{\text{exp}} - R_i^{\text{calc}})^2 \quad \dots (5.14)$$

where N is the total number of experiments at any given temperature, has been minimized. The calculated rate from a given model (R_i^{cal}) is a function of the unknown parameters. R_i^{exp} is the corresponding experimental rate.

Using these data (Table 2), the values of parameters in various models were calculated. For this, the RSS (objective function) is minimized by using Marquadt- Levenberg and Gauss-Newton techniques.

All the optimization programs are available in MATLAB ver. 4.0 (Optimization Tool-Box). The optimization subroutines are available in the form of m.files; viz, `leastsq.m` (for Marquadt Leivenberg) and `fsolve.m` (for Gauss-Newton).

Parameters were estimated for Models 1-6. at different temperatures of 500°C, 525°C and 550°C respectively. The values of parameters are reported in Table 3.

Models 1-4 gave large value of RSS. The coefficients were also negative. Although Model 6 gave low RSS, at temperatures of 500°C and 525°C it had negative rate coefficients. Only Model 5 had

positive rate coefficients and lowest RSS. Hence it is assumed that the most plausible model is Model 5.

Table 1. Rate expressions for various rate controlling steps

S.	Rate Controlling	Rate Equation	where
No. step	1	2	3
1.	$B + \sigma \xrightleftharpoons[k_{-1}]{k_1} B\sigma$	$-r_B = \frac{k_1' [p_B - K_7 \sqrt{p_A}]}{[1 + K_8 \sqrt{p_A}]}$	$K_7 = \frac{K_3}{K_1 K_2 K_4} \sqrt{\frac{K_6}{K_5}}$ $K_8 = \frac{K_3 (1+K_2)}{K_4 K_2} \sqrt{\frac{K_6}{K_5}}$ $k_1' = k_1 C_\sigma^O$
2.	$B\sigma \xrightleftharpoons[k_{-3}]{k_2} O\sigma$	$-r_B = \frac{k_2' [K_1 \rho_B - K_9 \sqrt{p_A}]}{[1 + K_1 \rho_B + K_{10} \sqrt{p_A}]}$	$K_9 = \frac{K_3}{K_2 K_4} \sqrt{\frac{K_6}{K_5}}$ $K_{10} = \frac{K_3}{K_4} \sqrt{\frac{K_6}{K_5}}$ $k_2' = k_2 C_\sigma^O$
3.	$O\sigma \xrightleftharpoons[k_{-3}]{k_3} O + \sigma$	$-r_B = \frac{k_3' [K_{12} \rho_B - K_{11} \sqrt{p_A}]}{[1 + K_1 \rho_B + K_{12} p_B]}$	$K_{11} = \frac{1}{K_3 K_4} \sqrt{\frac{K_6}{K_5}}$ $K_{12} = K_1 K_2$ $k_3' = k_3 C_\sigma^O$

Table 1 (contd.)

1	2	3	4
4.	$O + \tau \xrightleftharpoons[k_{-4}]{k_4} O\tau$	$-r_B = \frac{k_4' [K_{13}\rho_B - K_{14}\sqrt{p_A}]}{[1 + K_6\rho_A + K_{15}\sqrt{p_A}]}$	$K_{13} = \frac{K_1 K_2}{K_3}$ $K_{14} = \frac{1}{K_4} \sqrt{\frac{K_6}{K_5}}$ $K_{15} = \sqrt{\frac{K_6}{K_5}}$ $k_4' = k_4 C_\tau^O$
5.	$2O\tau \xrightleftharpoons[k_{-5}]{k_5} A\tau + \tau$	$-r_B = \frac{k_5' [K_{16}^2\rho_B^2 - \frac{K_6}{K_5} p_A]}{[1 + K_6\rho_A + K_{16}\sqrt{p_B}]^2}$	$K_{16} = \frac{K_1 K_2 K_4}{K_3}$ $k_5' = k_5 C_\tau^O$
6.	$A\tau \xrightleftharpoons[k_{-6}]{k_6} A + \tau$	$-r_B = \frac{k_6' [K_{17}\rho_B^2 - K_{18} p_A]}{[1 + K_{17}\rho_B^2 + K_{19} p_B]}$	$K_{17} = \frac{K_5 K_4^2 K_1^2 K_2^2}{K_3^2}$ $K_{18} = \frac{1}{K_6}$ $K_{19} = \frac{K_1 K_2 K_4}{K_3}$ $k_6' = k_6 C_\tau^O$

Table 2. Concentration of the species and rate of LPG depletion

Run No.	Temp. °C	Inlet Conc. of LPG x 10 ³ mol/l	Outlet Conc. of LPG x 10 ³ mol/l	Avg Partial press. of LPG x 10 ² atm	Avg Partial Press. of BTX x 10 ³ atm	Rate x 10 ² g mol/g.h
13	500	2.152	2.087	5	0.20	0.80
14		4.304	4.132	10	0.97	2.14
15		8.607	8.090	20	1.97	6.43
16		10.785	10.005	25	2.76	9.37
17		12.910	11.877	30	4.19	12.85
18	525	2.152	2.076	5	0.32	0.94
19		4.304	4.110	10	1.19	2.41
20		8.607	6.100	15	2.06	4.42
21		10.759	8.047	20	2.99	6.96
22		12.910	11.813	30	5.27	13.66
23	550	2.152	2.066	5	0.45	1.07
24		4.304	4.088	10	1.98	2.68
25		6.455	6.077	15	3.11	4.82
26		8.607	8.004	20	3.77	7.50
27		12.910	11.748	30	6.53	14.46

Table 3. Values of parameters and RSS for Model 1-6

Temp. °C	Model 1	Model 2	Model 3
500	$k'_1 = 0.36$	$k'_2 = 11.0$	$k'_3 = 7.334$
	$K_7 = 1.866$	$K_1 = 0.009$	$K_{12} = 0.044$
	$K_8 = -7.58$	$K_9 = 0.024$	$K_{11} = 0.0659$
		$K_{10} = 1.020$	$K_1 = -1.681$
	$RSS = 7.46 \times 10^{-6}$	$RSS = 1.02 \times 10^{-4}$	$RSS = 5.421 \times 10^{-6}$
525	$k'_1 = 0.3329$	$k'_2 = 18.27$	$k'_3 = 2.092$
	$K_7 = 1.3615$	$K_1 = 0.057$	$K_{12} = 0.3165$
	$K_8 = -7.365$	$K_9 = 0.1249$	$K_{11} = 0.606$
		$K_{10} = 3.000$	$K_1 = -0.458$
	$RSS = 5.56 \times 10^{-7}$	$RSS = 4.73 \times 10^{-6}$	$RSS = 2.56 \times 10^{-6}$
550	$k'_1 = 0.262$	$k'_2 = 60.41$	$k'_3 = 1.56$
	$K_7 = 0.745$	$K_1 = 0.0156$	$K_{12} = 0.228$
	$K_8 = -7.484$	$K_9 = 0.024$	$K_{11} = 0.1817$
		$K_{10} = 1.000$	$K_1 = -1.385$
	$RSS = 6.72 \times 10^{-7}$	$RSS = 3.6 \times 10^{-5}$	$RSS = 4.3 \times 10^{-4}$

contd.

Table 3. (contd.)

Temp. °C	Model 4	Model 5	Model 6
500	$k'_4=22.6$	$k'_5=0.467$	$k'_6=6.239$
	$K_{13}=0.70$	$K_{16}=2.715$	$K_{17}=0.2755$
	$K_{14}=-0.03$	$K_5=89.05$	$K_{18}=-1.2673$
	$K_{15}=0.017$	$K_6=33.46$	$K_{19}=1.4599$
	$K_6=-123.83$		
	$RSS=6.59 \times 10^{-6}$	$RSS=1.91 \times 10^{-6}$	$RSS=6.67 \times 10^{-6}$
525	$k'_4=4.778$	$k'_5=0.726$	$k'_6=76.81$
	$K_{13}=0.70$	$K_{16}=10.598$	$k_{17}=0.624$
	$K_{14}=0.3359$	$K_5=0.1529$	$K_{18}=2.886$
	$K_{15}=0.164$	$K_6=0.0003$	$K_{19}=83.80$
	$K_6=-2.3414$		
	$RSS=2.87 \times 10^{-6}$	$RSS=1.28 \times 10^{-6}$	$RSS=3.99 \times 10^{-6}$
550	$k'_4=15.19$	$k'_5=0.89$	$k'_6=44.82$
	$K_{13}=0.70$	$K_{16}=9.666$	$K_{17}=0.1463$
	$K_{14}=0.020$	$K_5=208.93$	$K_{18}=0.1208$
	$K_{15}=0.0234$	$K_6=1.995$	$K_{19}=8.93$
	$K_6=-77.4$		
	$RSS=1.93 \times 10^{-6}$	$RSS=1.1 \times 10^{-6}$	$RSS=1.43 \times 10^{-5}$

The activation energy was calculated by plotting $\ln k'_5$ vs $1/T$ (Figure 11). The activation energy came out to be 73.64 KJ/mol compared to 100 KJ/mol reported by Mao and Yao(1991) and 121 KJ/mol reported by Jana and Rao(1993a,b).

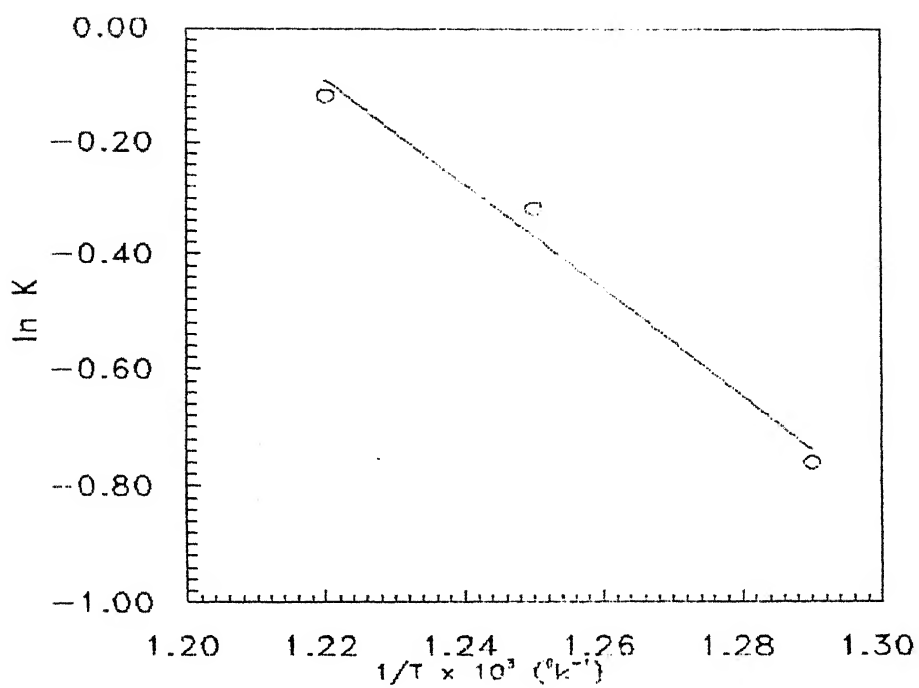


Fig11 . Temperature Dependence of the Logarithm of the Rate Constant of LPG Aromatization.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS.

6.1 CONCLUSIONS:

Conversion of LPG into aromatics has been studied using Zn-encilite catalysts. By analysis of product stream it was observed that butanes (iso-butane and n-butane) in LPG are more reactive than propane. Experimental studies have been conducted on conversion of butanes and propane, selectivity towards BTX, and yield of BTX. The parameters of experimental study have been chosen as temperature, contact time and concentration.

It was concluded from the study that as the temperature increases the amount of by products increases along with ~~the~~ the amount of BTX. Hence the selectivity decreases. Also there is a sharp increase in conversion as we increase the contact time. By studying the effect of concentration it was concluded that with increase in concentration the conversion increases.

The kinetic studies have been carried out in the temperature range of 500-550°C . This is the range for maximum yield of BTX. Experiments revealed that the rate controlling step was surface reaction(model 5). The model chosen for this study was derived from Langmuir-Hinshlwood model with dual site mechanism. The rate parameters were estimated using nonlinear regression algorithm. Confirmation was done with the trend shown by the kinetic constants with temperature.

The model that best fitted in our study is given by

$$-r_b = \frac{k_5' [k_{16}^2 p_b^2 - \frac{k_6}{k_5} p_a]}{[1 + k_6 p_a + k_{16} p_b]^2}$$

The calculated activation energy was found to be 73.64 KJ/mol.

6.2 Recommendations for future work

- (i) Detailed studies are recommended for Zn-encilite catalyst containing different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios,
- (ii) detailed characteristaion can be carried out using ESCA(electcron scattering for chemical analysis) to elucidate the chemical state of the Zn,
- (iii) coking mechanism for this reaction may be studied for the elucidation of mechanism of coking.

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APPENDIX A

Calculated values of calibration factors for GC

<u>Compounds</u>	<u>Calibration factors</u>
Nitrogen	1.03
Methane	1.00
Ethane+Ethene	1.85
Proopane	1.30
Propene	2.90
Iso-butane	0.90
N-butane	1.39
Benzene	1.12
Toluene	1.07
O-xylene	1.00
m-xylene	1.02
p-xylene	1.02

APPENDIX B

MODEL CALCULATION OF CONVERSION, SELECTIVITY AND YIELD

RUN NO 1

Molar flow rate of propane at inlet

$$= \frac{0.6738 \times 0.4 \times 80 \times 60 \times 1000}{22400} = 57.75 \text{ mg.mol/hr}$$

Molar flow rate of butanes (iso-butane+n-butane)

$$= \frac{0.2902 \times 0.4 \times 80 \times 60 \times 1000}{22400} = 24.87 \text{ mg.mol/hr}$$

From definition

$$\% \text{ conversion} = \frac{\text{no.of moles of propane/butane consumed}}{\text{no. of moles of propane/butane fed in LPG}} \times 100$$

$$\text{for propane} = \frac{57.75 - (0.5747 \times 85.71)}{57.75} \times 100 = 14.71 \%$$

$$\text{for butane} = \frac{24.87 - (0.1091 + 0.0634) \times 85.71}{24.87} \times 100 = 40.62 \%$$

$$\text{Total conversion} = \frac{(57.75 + 24.87) - (0.5747 + 0.1725) \times 85.71}{(57.75 + 24.87)} \times 100$$

$$= 22.52 \%$$

$$\% \text{ yield} = \frac{\text{no.of moles of BTX produced}}{\text{no.of moles of propane + butanes fed}} \times 100$$

$$= \frac{(0.0449 + 0.1033 + 0.0258) \times 85.71}{(57.75 + 24.87)} \times 100 = 18.05$$

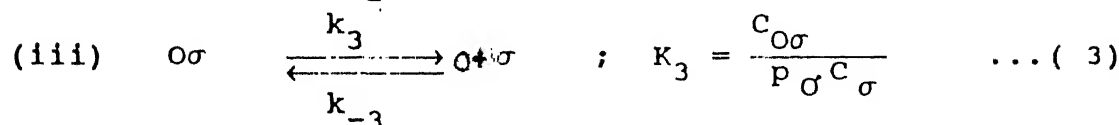
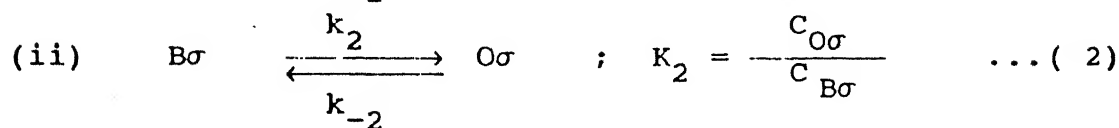
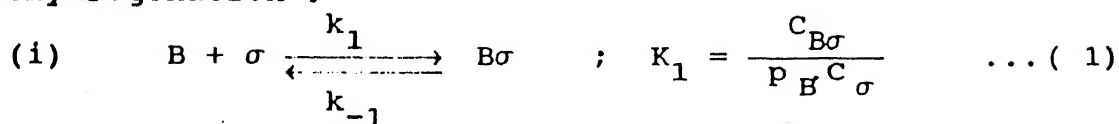
$$\% \text{ selectivity} = (18.05/22.52) \times 100 = 80.15$$

APPENDIX C

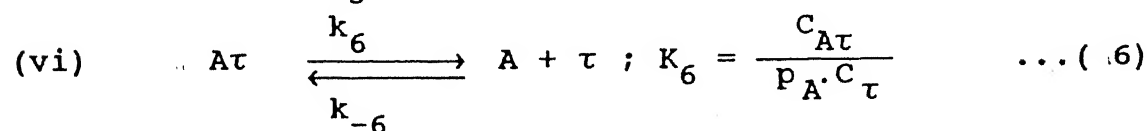
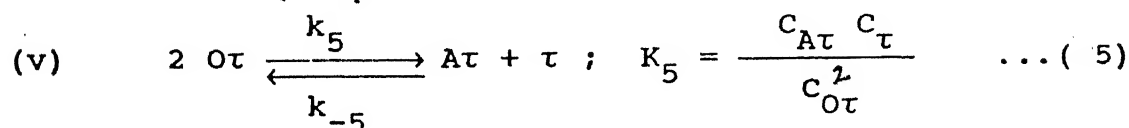
MODEL DERIVATION OF LANGMUIR-HINSHELWOOD MODEL

(Derivation of Model 5)

Dehydrogenation :



Aromatization :



where, B denotes n-butane
 O denotes butene
 A denotes aromatics
 σ denotes vacant acid sites

τ denotes vacant Zn^{2+} sites

then surface reaction is rate controlling. Rate of reaction of butane is given by

$$-r_B = k_5 C_{O\tau}^2 - k_{-5} C_{A\tau} C_\tau \quad \dots (7)$$

$$= \left[C_{O\tau}^2 - \frac{C_{A\tau} C_\tau}{K_5} \right] \quad \dots (8)$$

here, $K_5 = \frac{k_5}{k_{-5}}$, is surface reaction equilibrium constant

from reaction step (1) we have $\frac{C_{B\sigma}}{C_\sigma} = K_1 p_B$

from reaction step (2) we have $C_{O\sigma} = K_2 C_{B\sigma}$

from reaction step (3) we have $p_O = \frac{C_{O\sigma}}{K_3 C_\sigma}$

from above three equations we get,

$$p_O = \frac{K_1 K_2}{K_3} p_B$$

$$C_{A\tau} = K_6 p_A C_\tau$$

$$C_{O\tau} = K_4 p_O C_\tau$$

putting all the values in rate equations we get,

$$-r_B = k_5 \left[K_{16}^2 p_B^2 - \frac{K_6}{K_5} p_A \right] C_\tau^2 \quad \dots\dots\dots (9)$$

where,

$$K_{16} = \left[\frac{K_1 K_2 K_4}{K_3} \right]^2$$

for τ site balance we have

$$\begin{aligned} C_{\tau o} &= C_\tau + C_{O\tau} + C_{A\tau} \\ &= C_\tau [1 + K_4 p_O C_\tau + K_6 p_A C_\tau] \end{aligned}$$

by replacing the value of p_O

$$C_\tau = \left[\frac{C_{\tau o}}{1 + K_{16} p_B + K_6 p_A} \right]^2$$

putting it in the rate equations we finally get,

$$-r_B = \frac{k'_5 \left[K_{16}^2 p_B^2 - \frac{K_6}{K_5} p_A \right]}{\left[1 + K_{16} p_B + K_6 p_A \right]^2}$$

where

$$k'_5 = k_5 \times C_{\tau o}$$

Similarly, we can derive the equations for other models

APPENDIX D

REACTION RATE CALCULATIONS

Run no 13

$$\% \text{ of conversion} = \frac{C_{ai} - C_{ao}}{C_{ai}} \times 100$$

C_{ai} - Inlet concentration of propane and n-butane

C_{ao} - Outlet concentration of propane and n-butane

$$\begin{aligned} \text{Total molar flow rate of inlet feed} &= \frac{200 \times 60 \times 1000}{22400} \\ &= 535.71 \text{ mg.mol/hr} \end{aligned}$$

$$\text{Total molar flow rate of } N_2 = 0.95 \times 535.71 = 508.92 \text{ mg.mol/hr}$$

Total molar flow rate of propane and butanes at inlet

$$= (0.6738 + 0.1838 + 0.1064) \times 0.05 \times 535.71 = 25.82 \text{ mg.mol/hr}$$

$$C_{ai} = \frac{25.82 \times 1000}{200 \times 60} = 2.1517 \text{ mg.mol/lit}$$

$$C_{ao} = \frac{(0.6538 + 0.1783 + 0.1032) \times 1000 \times 26.79}{200 \times 60} = 2.088 \text{ mg.mol/lit}$$

$$\Delta X = \frac{C_{ai} - C_{ao}}{C_{ai}} \times 100$$

$$= \frac{2.1517 - 2.088}{2.1517} \times 100 = 2.96\%$$

$$\text{Reaction rate} = \frac{\Delta X}{(\Delta W/F_b)} = \frac{0.0296}{0.1/26.79} = 0.8 \times 10^{-2} \text{ gmmol/gm-hr}$$

APPENDIX E

Experimental data

Run no	1	2
Weight of catalyst	= 0.30 g	0.30 g
Reaction temperature	= 475 °C	500 °C
Flow rate of feed	= 80 ml/min	80 ml/min
LPG concentration	= 40 %	40 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 5.51	6.27
Mol % of ethane + ethylene	= 1.47	2.24
Mol % of propane	= 57.47	53.27
Mol % of propylene	= 0.37	0.45
Mol% of Iso-butane	= 10.91	9.53
Mol% of n-butane	= 6.31	5.50
Mol % of Benzene	= 4.49	5.69
Mol % of Toluene	= 10.33	13.64
Mol % of Xylene	= 2.58	3.41

Total flow rate (mg mol/h) = 85.71 mg mol/h 85.71 mg mol/h

Run no	3	4
Weight of catalyst	= 0.30 g	0.30 g
Reaction temperature	= 525 °C	550 °C
Flow rate of feed	= 80 ml/min	80 ml/min
LPG concentration	= 40 %	40 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 8.70	10.50
Mol % of ethane + ethylene	= 3.11	3.75
Mol % of propane	= 49.75	46.62
Mol % of propylene	= 0.62	0.75
Mol% of Iso-butane	= 8.14	7.23
Mol% of n-butane	= 4.70	4.18
Mol % of Benzene	= 6.25	6.74
Mol % of Toluene	= 14.99	16.18
Mol % of Xylene	= 3.75	4.05

Total flow rate (mg mol/h) = 85.71 mg mol/h 85.71 mg mol/h

Run no	5	6
Weight of catalyst	= 1.0 g	1.0 g
Reaction temperature	= 500 °C	500 °C
Flow rate of feed	= 60 ml/min	60 ml/min
LPG concentration	= 33.33 %	42.85 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 10.92	15.21
Mol % of ethane + ethylene	= 3.12	4.35
Mol % of propane	= 53.79	48.19
Mol % of propylene	= 1.56	2.17
Mol% of Iso-butane	= 6.96	5.34
Mol% of n-butane	= 4.02	3.09
Mol % of Benzene	= 4.91	5.41
Mol % of Toluene	= 11.78	13.00
Mol % of Xylene	= 2.95	3.25

Total flow rate (mg mol/h) 53.57 mg mol/h 68.86 mg mol/h

Run no	7	8
Weight of catalyst	= 1.0 g	1.0 g
Reaction temperature	= 500 °C	500 °C
Flow rate of feed	= 60 ml/min	60 ml/min
LPG concentration	= 61.13 %	75.62 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 19.27	23.46
Mol % of ethane + ethylene	= 5.50	6.70
Mol % of propane	= 42.06	36.62
Mol % of propylene	= 2.75	3.35
Mol% of Iso-butane	= 3.98	2.92
Mol% of n-butane	= 2.30	1.68
Mol % of Benzene	= 6.03	6.32
Mol % of Toluene	= 14.48	15.16
Mol % of Xylene	= 3.62	3.79

Total flow rate (mg mol/h) = 98.24 mg mol/h 121.53 mg mol/h

Run no	9	10
Weight of catalyst	= 0.30 g	0.50 g
Reaction temperature	= 500 °C	500 °C
Flow rate of feed	= 100 ml/min	100 ml/min
LPG concentration	= 40 %	40 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 6.45	8.55
Mol % of ethane + ethylene	= 2.31	3.06
Mol % of propane	= 54.47	50.31
Mol % of propylene	= 0.46	0.61
Mol% of Iso-butane	= 12.27	10.99
Mol% of n-butane	= 7.10	6.36
Mol % of Benzene	= 4.24	5.03
Mol % of Toluene	= 10.16	12.07
Mol % of Xylene	= 2.54	3.02

Total flow rate (mg mol/h) = 107.14 mg mol/h 107.14 mg mol/h

Run no	11	12
Weight of catalyst	= 0.20 g	1.0 g
Reaction temperature	= 500 ^o C	500 ^o C
Flow rate of feed	= 100 ml/min	100 ml/min
LPG concentration	= 40 %	40 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 10.50	12.73
Mol % of ethane + ethylene	= 3.75	4.55
Mol % of propane	= 60.16	43.00
Mol % of propylene	= 0.75	0.91
Mol% of Iso-butane	= 14.04	8.52
Mol% of n-butane	= 8.13	4.93
Mol % of Benzene	= 2.65	6.34
Mol % of Toluene	= 6.51	15.22
Mol % of Xylene	= 1.59	3.81

Total flow rate (mg mol/h) = 107.14 mg mol/h 107.14 mg mol/h

Run no	13	14
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 500 ^o C	500 ^o C
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 5%	10%

Product analysis (nitrogen free basis)

Mol % of Methane	= 4.27	4.54
Mol % of ethane + ethylene	= 1.53	1.63
Mol % of propane	= 65.38	64.70
Mol % of propylene	= 0.31	0.32
Mol% of Iso-butane	= 17.83	17.65
Mol% of n-butane	= 10.32	10.21
Mol % of Benzene	= 0.10	0.24
Mol % of Toluene	= 0.24	0.58
Mol % of Xylene	= 0.06	0.15

Total flow rate (mg mol/h) = 26.79 mg mol/h 53.57 mg mol/h

Run no	15	16
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 500°C	500°C
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 20 %	25 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 5.88	6.48
Mol % of ethane + ethylene	= 2.10	2.30
Mol % of propane	= 63.36	62.68
Mol % of propylene	= 0.42	0.46
Mol% of Iso-butane	= 17.28	17.09
Mol% of n-butane	= 10.00	9.89
Mol % of Benzene	= 0.25	0.28
Mol % of Toluene	= 0.59	0.66
Mol % of Xylene	= 0.15	0.17

Total flow rate (mg mol/h) = 107.16 mg mol/h 133.95 mg mol/h

Run no	17	18
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 500°C	525°C
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 30 %	5 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 6.94	4.43
Mol % of ethane + ethylene	= 2.48	1.58
Mol % of propane	= 62.01	65.02
Mol % of propylene	= 0.50	0.32
Mol% of Iso-butane	= 16.91	17.74
Mol% of n-butane	= 9.79	10.27
Mol % of Benzene	= 0.35	0.16
Mol % of Toluene	= 0.84	0.38
Mol % of Xylene	= 0.21	0.10

Total flow rate (mg mol/h) = 160.50 mg mol/h 26.79 mg mol/h

Run no	19	20
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 525°C	525°C

Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 10 %	15 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 4.73	5.27
Mol % of ethane + ethylene	= 1.69	1.88
Mol % of propane	= 64.37	63.67
Mol % of propylene	= 0.34	0.38
Mol% of Iso-butane	= 17.55	17.37
Mol% of n-butane	= 10.16	10.05
Mol % of Benzene	= 0.30	0.34
Mol % of Toluene	= 0.71	0.82
Mol % of Xylene	= 0.18	0.21

Total flow rate (mg mol/h)	= 53.57 mg mol/h	80.37 mg mol/h
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Run no	21	22
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 525 °C	525 °C
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 20 %	30 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 5.86	7.02
Mol % of ethane + ethylene	= 2.10	2.51
Mol % of propane	= 63.02	61.67
Mol % of propylene	= 0.42	0.50
Mol% of Iso-butane	= 17.19	16.82
Mol% of n-butane	= 9.95	9.74
Mol % of Benzene	= 0.38	0.44
Mol % of Toluene	= 0.90	1.06
Mol % of Xylene	= 0.23	0.26

Total flow rate (mg mol/h)	= 107.16 mg mol/h	169.5 mg mol/h
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Run no	23	24
Weight of catalyst	= 0.10 g	0.10 g
Reaction temperature	= 550 °C	550 °C
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 5 %	10 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 4.59	4.51
Mol % of ethane + ethylene	= 1.64	1.61
Mol % of propane	= 64.70	64.03
Mol % of propylene	= 0.33	0.32

Mol% of Iso-butane	= 17.64	17.46
Mol% of n-butane	= 10.21	10.11
Mol % of Benzene	= 0.23	0.50
Mol % of Toluene	= 0.54	1.19
Mol % of Xylene	= 0.14	0.30

Total flow rate (mg mol/h) = 26.79 mg mol/h 53.57 mg mol/h

Run no	25	26
Weight of catalyst	= 0.10 ^o g	0.10 ^o g
Reaction temperature	= 550 ^o c	550 ^o c
Flow rate of feed	= 200 ml/min	200 ml/min
LPG concentration	= 15 %	20 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 5.12	5.92
Mol % of ethane + ethylene	= 1.83	2.12
Mol % of propane	= 63.36	62.68
Mol % of propylene	= 0.37	0.42
Mol% of Iso-butane	= 17.28	17.09
Mol% of n-butane	= 10.00	9.89
Mol % of Benzene	= 0.52	0.47
Mol % of Toluene	= 1.24	1.13
Mol % of Xylene	= 0.31	0.28

Total flow rate (mg mol/h) = 80.37 mg mol/h 107.16 mg mol/h

Run no	27
Weight of catalyst	= 0.10 ^o g
Reaction temperature	= 550 ^o c
Flow rate of feed	= 200 ml/min
LPG concentration	= 30 %

Product analysis (nitrogen free basis)

Mol % of Methane	= 7.06
Mol % of ethane + ethylene	= 2.53
Mol % of propane	= 61.33
Mol % of propylene	= 0.50
Mol% of Iso-butane	= 16.73
Mol% of n-butane	= 9.68
Mol % of Benzene	= 0.55
Mol % of Toluene	= 1.31
Mol % of Xylene	= 0.33

Total flow rate (mg mol/h) = 160.5 mg mol/h